Short communication

Evaluation of various additives on the preparation of rice husk ash (RHA)/CaO-based sorbent for flue gas desulfurization (FGD) at low temperature

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ABSTRACT

This paper examines the effectiveness of 10 additives toward improving SO_2 sorption capacities (SSC) of rice husk ash (RHA)/lime (CaO) sorbent. The additives examined are NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$. Most of the additives tested increased the SSC of RHA/CaO sorbent, whereby NaOH gave highest SSC (30 mg SO_2/g sorbent) at optimum concentration (0.25 mol/l) compared to other additives examined. The SSC of RHA/CaO sorbent prepared with NaOH addition was also increases from 17.2 to 39.5 mg SO_2/g sorbent as the water vapor increases from 0% RH to 80% RH. This is probably due to the fact that most of additives tested act as deliquescent material, and its existence increases the amount of water collected on the surface of the sorbent, which played an important role in the reaction between the dry-type sorbent and SO_2. Although most of the additives were shown to have positive effect on the SSC of the RHA/CaO sorbent, some were found to have negative or insignificant effect. Thus, this study demonstrates that proper selection of additives can improve the SSC of RHA/CaO sorbent significantly.

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1. Introduction

Acid rain and the acidification of the environment has emerged as a serious global problem during recent decades. Sulfur dioxide (SO_2), represents 98% of the sulfur oxide pollutants generated mainly from large-scale fossil fuel combustion, is commonly accepted as the most important precursor to acid rain [1,2]. The removal of SO_2-containing gasses has received considerable attention in recent decades due to a variety of effects caused by this pollutant. Dry sorbent injection control technologies is among the general method which has been widely accepted by reason of being simple with less equipment, lower capital and operating costs, limited secondary waste generation, and fewer problems of corrosion and scaling-up [3–5]. Nevertheless, acid gas sorption capacities are generally lower than those achieved with wet control technologies. Therefore, enhancing the sorption capacities of dry sorbent toward SO_2 has been an important issue for dry-type methods application.

There are a number of dry-type sorbents that have been considered in the literature for usage in desulfurization process. Previously, we have reported the preparation of siliceous/calcium dry-type sorbents prepared from coal fly ash [6,7], oil palm ash [8,9]

and rice husk ash [10]. It was found that, those prepared sorbent have higher SO_2 sorption capacity (SSC) relating to higher surface areas due to the fact that coal fly ash, oil palm ash and rice husk ash are a pozzolanic material (mainly consist of SiO_2/Al_2O_3). These pozzolanic materials can react with Ca-based in the presence of water to form calcium silicate hydrates (near-amorphous/poorly crystallized compounds) which have a very high surface area. Apart from that, the structural properties and sorption capacities of these types of sorbents are also affected by siliceous material/Ca-based ratio and the hydration conditions. Among those sorbents prepared, rice husk ash (RHA)/CaO sorbent shows highest SSC. However, our recent study on RHA/CaO sorbent [11] revealed that higher SSC did not show any correlation with specific surface area. On the other hand, many studies indicate that relative humidity has the greatest impact on the SSC of dry Ca-based sorbents at low temperature [12–17]. The relative humidity is consecutively connected to moisture content of the solids. In addition, some additives have been employed to alter the moisture content on the prepared sorbent surface in equilibrium with a gas phase of a given relative humidity [18–23]. Thus, the use of additive would then be expected to improve the sorbent SSC in desulfurization processes in the way of altering the sorbent particle's physical/chemical properties. Therefore, the scope of this work is to evaluate the effectiveness of various additives in the preparation of RHA-based sorbent for desulfurization process at low temperature.

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2. Experimental

2.1. Preparation of sorbent

The sorbents were prepared from RHA, lime (CaO) and different type of additives. The RHA was collected directly from Kilang Beras & Minyak Sin Guan Hup Sdn.Bhd., Nibong Tebal, Malaysia. Prior to use, the RHA was sieved to produce less than 200 μm particle size. The chemical composition of RHA is 68.0% SiO_2, 2.30% K_2O, 1.20% P_2O_5, 0.71% MgO, 0.59% CaO, 0.32% SO_3, 0.32% Cl_2O, 0.16% Al_2O_3, 0.40% others and 26.0% LOI (Loss On Ignition). Whereas, the additives examined in this investigation include NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$.

Sorbent was prepared by water hydration method [5]. Based on the optimum hydration conditions reported in our previous studies [11], sorbent was prepared in 250 ml conical flask by slurrying RHA and CaO (at a weight ratio of 2.5) in an aqueous solution containing the desired additive. Then the conical flask was inserted into a shaking water bath at 65 °C with a rotating stirring rate of 150 rpm for a specified time. After that, the slurry was then filtered and dried at 110 °C for 4 h. The sorbents were then pelletized, crushed and sieved to obtain the required particle size range of 250–300 μm.

2.2. Activity test for SO_2 sorption (SSC) study

The SSC of the sorbents was tested in a fixed-bed reactor (0.8 cm ID) fitted in a furnace for isothermal operation. During the study, 0.5 g of sorbent was filled in the center of the reactor (supported by 0.05 g of borosilicate glass wool). Feed flue gas containing SO_2 (2000 ppm), NO (500 ppm), O_2 (10%), water vapor (0–80%) and N_2 as the balance was subsequently passed through the sorbent at a reaction temperature of 87 °C. The total flow rate of the gas stream was controlled at 150 ml/min using mass flow controllers. The concentration of the SO_2 in the flue gas was measured using Portable Flue Gas Analyzer IMR 2800P before and after the sorption process. The schematic diagram and details of the experimental rig is presented in our previous study [6–8]. The SSC of the sorbent is expressed by the weight of SO_2 captured from the flue gas per gram sorbent [19]. In this study, only the data during 100% SO_2 removal was calculated to express SSC of the sorbent.

Every experimental run was repeated at least three times to increase the precision of the results, and only the average value was reported. The reproducibility of the experimental data was found to be sufficiently high with relative error between repeated runs was less than 5%.

2.3. Chemical and physical analysis

The chemical composition of RHA was analyzed using Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer. The scanning electron microscopy (SEM) examinations were performed with Leo Supra 35 VP Scanning Electron Microscope. X-ray diffraction (XRD) spectrum was recorded on a Siemens D5000 X-ray diffractometer to determine the phases present in the sorbent in the range of diffraction angle (2θ) 10–70° at a sweep rate of 1°/min. The Fourier transform infrared (FTIR) spectrum was carried out on a PerkinElmer FTIR 2000 spectrometer over the frequency range of 4000–400 cm^{-1}.

3. Results and discussion

3.1. Effect of different type of additives

Fig. 1 shows the effect of different type of additives used in the preparation of RHA/CaO sorbent. With an additives concentration
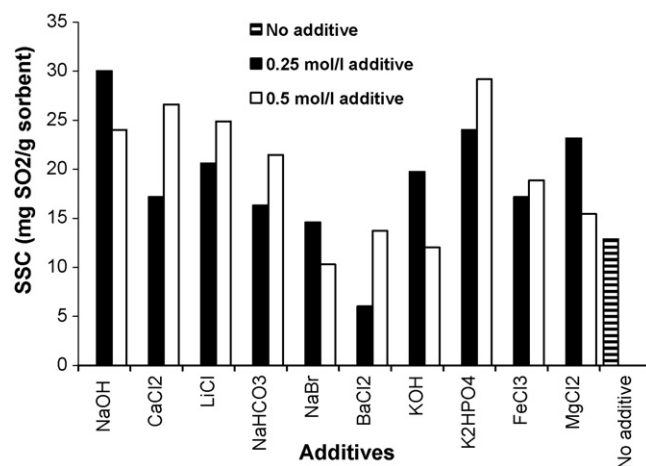

Fig. 1. Effect of various additives on SSC of RHA-based sorbent during 100% SO_2 removal.

of 0.25 mol/l, most of the sorbents were successful in increasing the sorption capacities of RHA/CaO sorbent toward SO_2 as compared to sorbent without additive. However, some of additives do not perform well such as $NaHCO_3$ and NaBr whereby SSC are about the same as sorbent prepared without additive. Apart from that, instead of giving negative effect on SSC of sorbent, the addition of $BaCl_2$ does not have any beneficial effect at all. As the concentration of additive increase to about 0.5 mol/l, the SSC of the sorbent prepared with the addition of $CaCl_2$, LiCl, $NaHCO_3$, $BaCl_2$, K_2HPO_4 and $FeCl_3$ also increases significantly. Nevertheless, for some additives such as NaOH, NaBr, KOH and $MgCl_2$, the results were different. At higher concentration (above 0.25 mol/l), these additives cause the SSC of RHA/CaO sorbent to decrease. This result reflects that there is an optimum additive concentration during the sorbent preparation that favors high sorbent SSC. From the viewpoint of additive addition to RHA/CaO sorbent SSC, NaOH gave better enhancement effect. Sorbent prepared with NaOH addition exhibited the highest SSC (30 mg SO_2/g sorbent) at optimum concentration (0.25 mol/l) compared to other additives examined.

In the addition of additive to RHA/CaO sorbent, the hydroxide of the cation plays a crucial role. The cation of additive should be very soluble for the sorbent to be effective [24]. Apart from that, the beneficial effect of additive addition is supposedly due to the presence of additive that might increase the dissolution rate of silica from RHA. The increase in the dissolution of silica will ultimately increase the formation of Si–Ca complex that has a high SSC [5–9,25]. However, the XRD pattern of sorbents prepared with the addition of NaOH (shown in Fig. 2) exhibited different results when compared with RHA/CaO sorbent without NaOH addition. Only characteristic peak of calcium carbonate ($CaCO_3$) was detected at $2\theta = 29.39°$ and 39.39°. Apart from that, a weak peak corresponding to unreacted amorphous silica was also observed at $2\theta = 35.96°$ and 48.60° for sorbent prepared with NaOH. On the other hand, more phases were detected in the sorbent prepared without the addition of additive, such as $Ca_2SiO_4 \cdot H_2O$ ($2\theta = 25.16°/27.32°$), $Ca_3Si_2O_7$ ($2\theta = 38.01°/46.09°/50.42°$) and $Ca_3Al_2Si_3O_{12}$ ($2\theta = 37.22°/47.46°/57.70°/60°$). This result indicates that both sorbents prepared with NaOH contained much less of these Si–Ca complex phases. In addition, the reaction between silica and CaO during the hydration process has somehow been inhibited by the existence of additive. This might be due to the fact that NaOH is a strong alkaline and the dissolution of CaO was limited by the common ion effect [19].
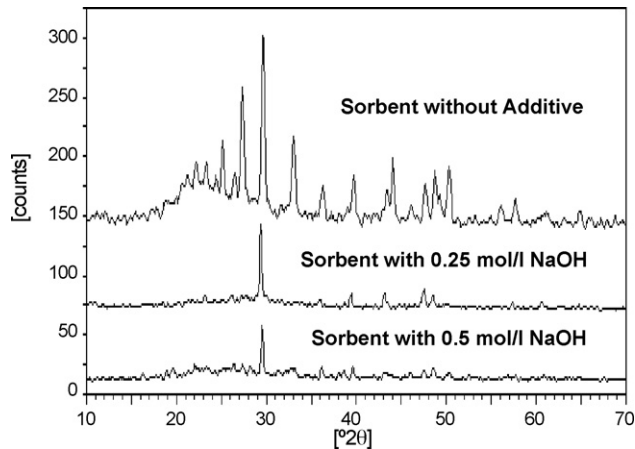
Fig. 2. XRD pattern of RHA/CaO sorbent with and without NaOH.

The sorbents prepared with NaOH addition was further subjected to FTIR analysis to characterize specific functional group. It was observed from Fig. 3 that there was no distinct FTIR spectrum pattern for both sorbents prepared before subjected to humidified flue gas. The spectrums (Fig. 3a and b) showed the prepared sorbents were mainly composed of carbonate (CO_3^{2-}) due to a broad band near $1450\,cm^{-1}$ and a sharp band near 875 and $712\,cm^{-1}$ [26,27]. A sharp vibration band approximately at $3640\,cm^{-1}$ usually caused by the stretching of CaO–H [25]. The bands around 460–$470\,cm^{-1}$ (Si–O–Si band) and $795\,cm^{-1}$ (Si–O–Si symmetric strength) are observed for amorphous silica. However, Si–O–Si asymmetric bands which usually near $1100\,cm^{-1}$ is not detected [28–32]. A broad band situated around $1050\,cm^{-1}$ is assigned to Si–O–C stretch [33]. Moreover, the band around $3450\,cm^{-1}$ is typically caused by hydroxyl groups or adsorbed water due to O–H stretches. Since the sorbent was prepared from RHA, this also can be caused by silanol groups [30,32]. In contrast, after both sorbents subjected to feed gas (Fig. 3c and d), the vibration peaks of CO_3^{2-} become weaker, which indicated the amount of carbonate decreased. Furthermore, the products of the desulfurization reaction, mainly sulfate (SO_4^{2-}) species, is characterized by a broad bands due to S–O stretching near 1050–$1100\,cm^{-1}$, S–O bending at $670\,cm^{-1}$ and a single peak close to $1640\,cm^{-1}$ related to hydroxyl

groups (O–H bending) [30,34]. The relative intensity of hydroxyl groups displayed an obvious increase due to hygroscopic properties of prepared sorbent, which adsorb more water from humidified flue gas and thus enhance SSC. These O–H bands also exhibited a different degree of hydration for the water molecules in the crystal lattice structure. Additionally, a slight/weak band around $970\,cm^{-1}$ is detected for sulfite (SO_3^{2-}) species [33,35].

3.2. Effect of relative humidity

It was well-known that the reaction which involves SO_2 and dry-type sorbent at low temperature proceeds under the presence of appreciable amount of water vapor. The effect of water vapor (relative humidity, RH) on the SSC of RHA/CaO sorbent with various type of additive addition is shown in Fig. 4. From experimental results, it was found that RH exerted significant influence on the sorbent SSC. When the reaction was carried out under dry condition (0% RH), the maximum sorbent SSC was only found to be capable of achieving 20 min of 100% SO_2 removal (SSC = 17.2 mg SO_2/g sorbent), *i.e.* using NaOH as an additive. However, after introducing water vapor (RH) from humidified flue gas, most the sorbent SSC increases drastically with relative humidity. In contrast, the addition of NaBr and K_2HPO_4 showed only slightly increase in SSC, while $NaHCO_3$ is the only additive that caused the sorbent SSC to decrease when the RH of the activity test was increase from 50% to 80%.

In all cases, the addition of NaOH still gave the maximum SSC. The SSC of RHA/CaO sorbent prepared with NaOH addition increases from 30 to 39.5 mg SO_2/g sorbent as the water vapor increases from 50% RH to 80% RH. The positive effect of RH on the SSC of the sorbent was due to the water adsorbed and/or collected on the sorbent surface which played an important role in the reaction between the dry-type sorbent and SO_2. Furthermore, with the presence of additives the water sorption capacities of sorbents also increase since most of additives tested act as deliquescent material (*i.e.* highly hygroscopic substances). At the same time the Ca-based compound in the interior of the RHA particle become more accessible to SO_2. As can be seen from scanning electron micrograph (SEM) analysis (Fig. 5), after subjected to humidified flue gas, particle size of the sorbents significantly increase (at the same magnification, $100\times$). The larger particle size of the sorbent could be due to the agglomerating of smaller particles during the desulfurization reaction. It was also observed that the particles of sorbents containing additive have a wet-look as compared with sorbent prepared without additive which have a dry-look and the particles are more loose. Furthermore, it has been reported by Ho et al. [14] and Liu et al. [16]

Fig. 4. Effect of relative humidity on SSC of RHA-based sorbent with different type of additives during 100% SO_2 removal.
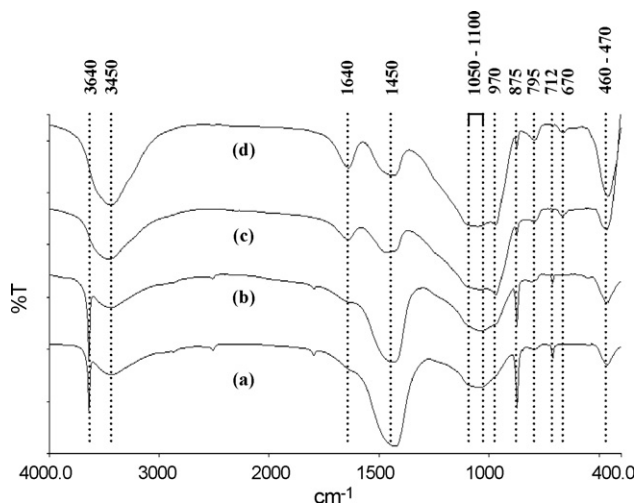

Fig. 3. Transmittance IR spectra of prepared sorbent with (a) 0.25 mol/l NaOH; (b) 0.5 mol/l NaOH; and sorbents after subjected to humidified flue gas for (c) 0.25 mol/l NaOH; (d) 0.5 mol/l NaOH addition.
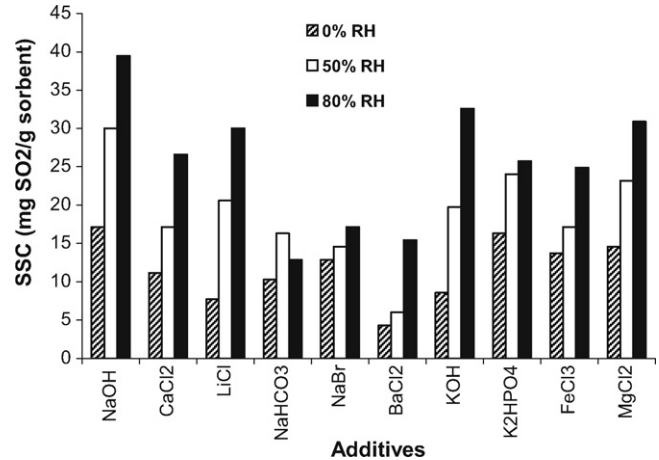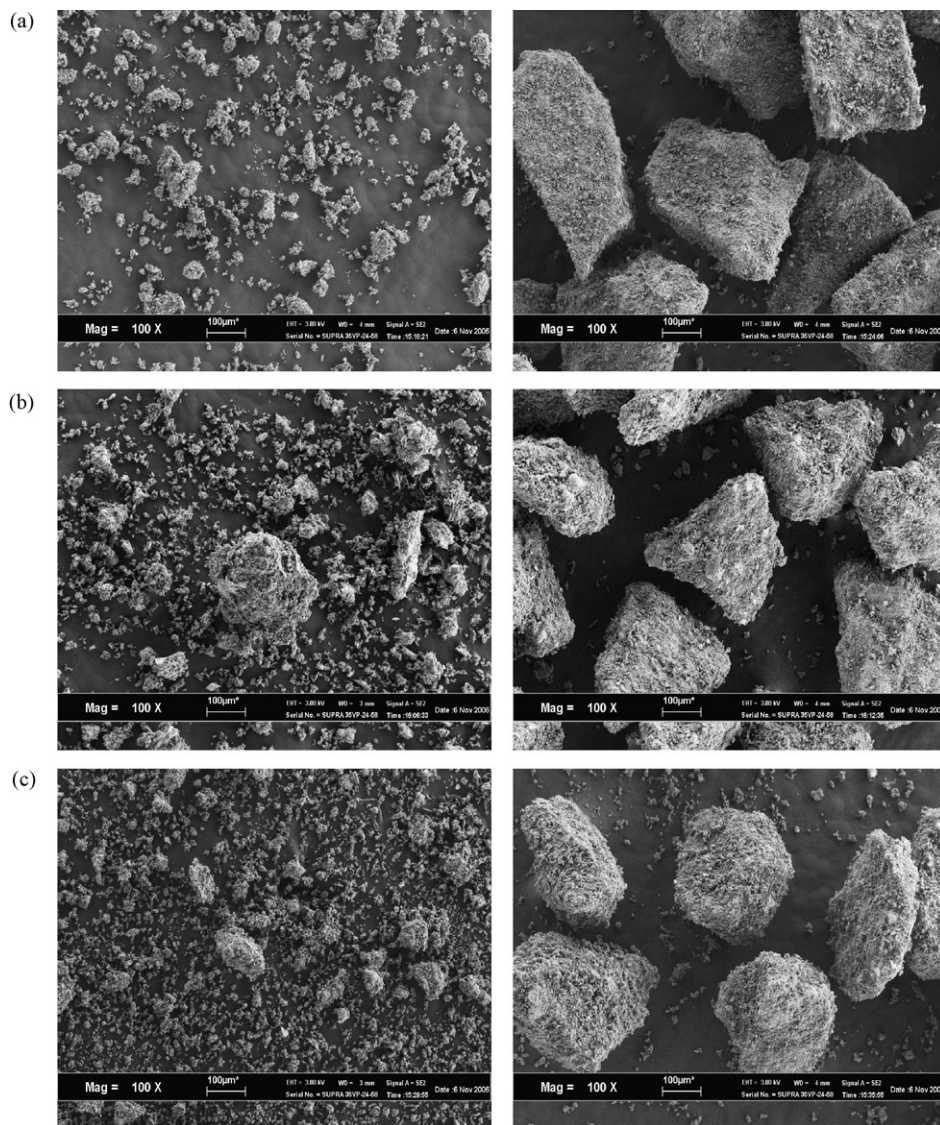
Fig. 5. SEM micrograph of RHA/CaO sorbents prepared with the addition of (a) NaOH, (b) KOH and (c) CaCl$_2$ before and after subjected to humidified flue gas at 80% RH.

that the reaction of SO$_2$ with Ca-containing sorbents at low temperature requires the presence of water on the surface of sorbent particles and the extent of reaction increases with an increasing amount of water adsorbed.

4. Conclusions

Most of the additives employed in RHA/CaO sorbent exhibit a higher SSC than sorbent without additive. The most reactive sorbent for SO$_2$ removal was prepared by slurrying RHA/CaO with NaOH. The SSC of RHA/CaO sorbent prepared with NaOH addition increases from 30 to 39.5 mg SO$_2$/g sorbent as the water vapor increases from 50% RH to 80% RH. The beneficial effect of additives depends on the concentration of additive and the water vapor (relative humidity).

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